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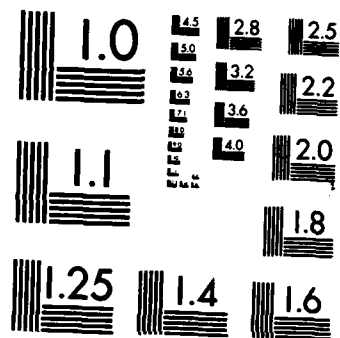
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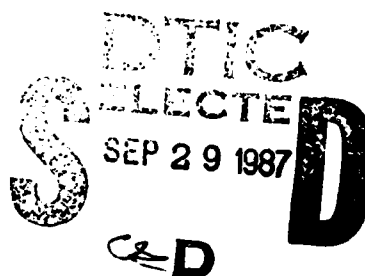
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***EQUILIBRIUM ANALYSIS OF THE
PREPARATION OF $In_xGa_{1-x}As$ BY THE
VPE-HYDRIDE TECHNIQUE; METHOD
TO PREDICT THE COMPOSITION OF
THE TERNARY***

Kenneth P. Quinlan



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1. INTRODUCTION

Epitaxial layers of $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ have electrical properties that make them important materials for microwave and optoelectronic devices.¹⁻⁴ Epitaxial growth of $\text{In}_x\text{Ga}_{1-x}\text{As}$ has been accomplished by various techniques: VPE-chloride,⁵ VPE-hydride,⁶ MOCVD,⁷ MBE⁸ and LPE.⁹ The versatility and advantages of the VPE-hydride method have been aptly described by Olsen and Zamerowski.¹⁰ Macrander and Strege¹¹ have demonstrated that $\text{In}_x\text{Ga}_{1-x}\text{As}$ epitaxial layers of excellent quality can be prepared by the VPE-hydride technique. The VPE-hydride technique will undoubtedly be applied more frequently to prepare III-V semiconductor devices.

Equilibrium models for the deposition of $\text{In}_x\text{Ga}_{1-x}\text{As}$ have been reported by various investigators. The primary objective of these equilibrium studies is to give the investigators a better estimate of the initial partial pressures of the reactants to produce a desired composition of the epitaxial layer. Many of these approaches are complicated and require a computer code for the calculation of the equilibrium of the multiphase system. The papers of Nagai et al¹² and Minagawa et al¹³ are examples of these techniques applied to the growth of $\text{In}_x\text{Ga}_{1-x}\text{As}$. Less

(Received for publication 12 December 1986)

(Due to the large number of references cited above, they will not be listed here.
See References, page 15.)

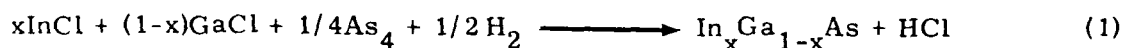
complicated methods for the deposition of $\text{In}_x\text{Ga}_{1-x}\text{As}$ have been reported by Kajiyama,¹⁴ Nagai¹⁵ and Jacobs et al.¹⁶ However, these methods required assignment of arbitrary values to the initial partial pressures or iterative procedures to determine the composition of the epitaxial layer.

A simplified method has been developed in the present study where the equilibrium expression can be used directly to analyze the reactor system performance, for example, composition of epitaxial layer, effect of arsine pressure on composition, and so on. Evaluation of the equilibrium expressions requires values of the amounts of $\text{In}_x\text{Ga}_{1-x}\text{As}$ deposited to be known. Values of $\text{In}_x\text{Ga}_{1-x}\text{As}$ deposited at three arsine pressures were determined from previously reported data. A linear plot of the initial concentrations of arsenic ($P_{\text{As}_4}^0$) versus amounts of deposit expressed in atmospheres allows the determination of $P_{\text{In}_x\text{Ga}_{1-x}\text{As}}$ at various initial arsenic concentrations. The fairly consistent agreement achieved between the experimental values of other investigators and the present approach indicates the method is useful in estimating the composition and in understanding the $\text{In}_x\text{Ga}_{1-x}\text{As}$ deposition system.

2. EQUILIBRIUM ANALYSIS

In the present study of the equilibrium analysis only the following species are considered: InCl , GaCl , As_4 , HCl , H_2 , and $\text{In}_x\text{Ga}_{1-x}\text{As}$. Other probable species exist only in minor amounts.^{17, 18}

The overall equation for the deposition of $\text{In}_x\text{Ga}_{1-x}\text{As}$ in the VPE-hydride method is depicted in Eq. (1):



14. Kajiyama, K. (1976) Vapor pressure dependence of the relative composition of III-V mixed crystals in vapor-phase epitaxy, J. Electrochem. Soc. 123:423.
15. Nagai, H. (1979) A simple analysis of vapor-phase growth; citing an instance of $\text{Ga}_x\text{In}_{1-x}\text{As}$, J. Electrochem. Soc. 126:1401.
16. Jacobs, K., Simon, I., Bugge, F., and Butter, E. (1984) A simple method for calculation of the composition of the VPE grown $\text{Ga}_x\text{In}_{1-x}\text{As}$ layers as a function of growth parameters, J. Crystal Growth 69:155.
17. Ban, V. S. (1972) Mass spectrometric and thermodynamic studies of the CVD of some III-V compounds, J. Crystal Growth 17:19.
18. Ban, V. S., and Ettenberg, M. (1973) Mass spectrometric and thermodynamic studies of vapor-phase growth of $\text{In}_{1-x}\text{Ga}_x\text{P}$, J. Phys. Chem. Solids, 43:1119.

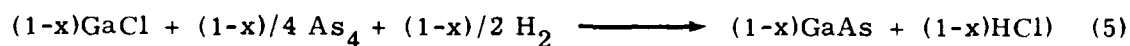
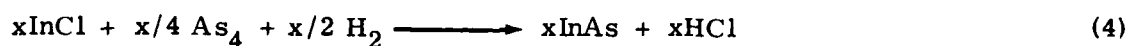
where x varies from 0 to 1. The equilibrium expression for Eq. (1) is

$$K_1 = \frac{a_{\text{In}_x\text{Ga}_{1-x}\text{As}} \cdot P_{\text{HCl}}}{P_{\text{InCl}}^x \cdot P_{\text{GaCl}}^{1-x} \cdot P_{\text{As}_4}^{1/4} \cdot P_{\text{H}_2}^{1/2}} \quad (2)$$

where a is the activity and the P 's are the equilibrium partial pressures. Since $\text{In}_x\text{Ga}_{1-x}\text{As}$ can be considered a pure chemical solid, its activity may be taken as one.¹⁹ Equation (2) reduces to Eq. (3):

$$K_1 = \frac{P_{\text{HCl}}}{P_{\text{InCl}}^x \cdot P_{\text{GaCl}}^{1-x} \cdot P_{\text{As}_4}^{1/4} \cdot P_{\text{H}_2}^{1/2}} \quad (3)$$

The equilibrium constant, K_1 , can be shown to be the product of the equilibrium constants for the formation of the binaries. The equations for the binary formation (InAs and GaAs) and their equilibrium expressions are depicted in Eqs. (4) and (5) respectively:



$$K_2 = \frac{a_{\text{InAs}}^x \cdot P_{\text{HCl}}^x}{P_{\text{InCl}}^x \cdot P_{\text{As}_4}^{x/4} \cdot P_{\text{H}_2}^{x/2}} \quad (6)$$

$$K_3 = \frac{a_{\text{GaAs}}^{1-x} \cdot P_{\text{HCl}}^{1-x}}{P_{\text{GaCl}}^{1-x} \cdot P_{\text{As}_4}^{(1-x)/4} \cdot P_{\text{H}_2}^{(1-x)/2}} \quad (7)$$

InAs and GaAs in Eqs. (4) and (5) are pure chemical substances and therefore their activities in Eqs. (6) and (7) may also be taken as one. The product of Eqs. (6) and (7) is therefore

$$K_2 K_3 = \frac{P_{\text{HCl}}}{P_{\text{InCl}}^x \cdot P_{\text{GaCl}}^{1-x} \cdot P_{\text{As}_4}^{1/4} \cdot P_{\text{H}_2}^{1/2}} \quad (8)$$

19. Klotz, I.M. (1950) Chemical Thermodynamics, Prentice-Hall, Inc., p. 268.

The right hand sides of Eqs. (3) and (8) are identical and therefore K_1 is equal to $K_2 K_3$.

The equilibrium values of the reactants and products in Eq. (8) [or (3)] may be defined in terms of the initial partial pressures and the amount of $\text{In}_x\text{Ga}_{1-x}\text{As}$ deposited expressed in atmospheres. The following relations give the material balances for the equilibrium partial pressures in Eq. (8).

$$P_{\text{HCl}} = P'_{\text{HCl}} + P_{\text{In}_x\text{Ga}_{1-x}\text{As}} \quad (9)$$

where P'_{HCl} is the partial pressure of the residual hydrogen chloride that remains after the reaction of HCl with indium and gallium in the source zones.

$P_{\text{In}_x\text{Ga}_{1-x}\text{As}}$ is equivalent to the HCl produced in Eq. (1). Values for P_{InCl}^x , P_{GaCl}^{1-x} and $P_{\text{As}_4}^{1/4}$ are

$$P_{\text{InCl}}^x = (P_{\text{InCl}}^0 - xP_{\text{In}_x\text{Ga}_{1-x}\text{As}})^x \quad (10)$$

$$P_{\text{GaCl}}^{1-x} = (P_{\text{GaCl}}^0 - (1-x)P_{\text{In}_x\text{Ga}_{1-x}\text{As}})^{1-x} \quad (11)$$

$$P_{\text{As}_4}^{1/4} = (P_{\text{As}_4}^0 - 1/4 P_{\text{In}_x\text{Ga}_{1-x}\text{As}})^{1/4} \quad (12)$$

where P^0 's are the initial partial pressures.

The only variable in the above equations that needs to be known to calculate the equilibrium partial pressures is the amount of $\text{In}_x\text{Ga}_{1-x}\text{As}$ ($P_{\text{In}_x\text{Ga}_{1-x}\text{As}}$) deposited. Values of the variable ($P_{\text{In}_x\text{Ga}_{1-x}\text{As}}$) at three different As_4 pressures were determined from the data of Weyburne and Quinlan.²⁰ The study showed that only one value of the $\text{In}_x\text{Ga}_{1-x}\text{As}$ deposit was necessary to describe the experimental data at each arsenic pressure. A plot of $P_{\text{In}_x\text{Ga}_{1-x}\text{As}}$ versus initial arsenic pressures ($P_{\text{As}_4}^0$) gave a linear relation that enables values of $P_{\text{In}_x\text{Ga}_{1-x}\text{As}}$ to be determined at any arsine pressure. The procedure and results are described in

20. Weyburne, D. W., and Quinlan, K. P. (1985) The Effects of Arsine Pressure on the Compositions, Carrier Concentrations, Mobilities and Growth Rates of Epitaxial Layers of $\text{Ga}_{1-x}\text{In}_x\text{As}$ Prepared by the VPE-Hydride Technique.

RADC-TR-85-238, AD A165278, Rome Air Development Center, Air Force Systems Command, Griffiss Air Force Base, NY. 13441-5700

the following section. The initial partial pressure of hydrogen, P_{H_2} , is used in Eq. (8) since the final pressure does not differ significantly from the initial pressure.

3. RESULTS AND DISCUSSION

The determination of the composition of $In_xGa_{1-x}As$ prepared by the VPE-hydride technique can be accomplished with the expanded form of Eq. (8) as presented in Eq. (13)

$$K_2 K_3 = \frac{P_{HCl} + P_{In_xGa_{1-x}As}}{(P_{InCl}^0 - xP_{In_xGa_{1-x}As})^x (P_{GaCl}^0 - (1-x)P_{In_xGa_{1-x}As})^{1-x} (P_{As_4}^0 - 1/4 P_{In_xGa_{1-x}As})^{1/4} P_{H_2}^{1/2}} \quad (13)$$

where x and $1-x$ are the mole fractions of indium arsenide and gallium arsenide, respectively. The terms in Eq. (13) have been defined in the preceding section. P_{InCl}^0 and P_{GaCl}^0 , the initial partial pressures of the Group III-monochlorides, were calculated from the starting hydrogen chloride pressure in the Group III-element source zones and the equilibrium constants for the following reactions:



Values for the equilibrium constants of reactions (14) and (15) were calculated from the thermodynamic data of Seki et al.²¹ and Kirwan,²² respectively. P_{HCl}' , the residual HCl from Reactions (14) and (15), was determined from the difference between the starting HCl pressures and the III-monochlorides. The P_{As}^0 was 1/4 of the initial arsine partial pressure. K_2 and K_3 were determined from the thermodynamic relationships derived by Jacobs et al.¹⁶ Values of $P_{In_xGa_{1-x}As}$ were found by determining those values of $P_{In_xGa_{1-x}As}$ in Eq. (13) that gave the best fit to describe the data of Weyburne and Quinlan²⁰ at the three arsine pressures.

21. Seki, H., and Minagawa, S. (1972) Equilibrium computation for the vapor growth of $In_xGa_{1-x}P$ crystals, Japan J. Appl. Phys. 11:850.

22. Kirwan, D.J. (1970) Reaction equilibria in the growth of GaAs and GaP by the chloride transport process, J. Electrochem. Soc. 117:1572.

Figures 1, 2 and 3 show the calculated curves with the experimental data of Weyburne and Quinlan²⁰ at the three arsenic pressures ($P_{As_4}^0$). The solid lines were calculated with Eq. (13) using values of $P_{In_xGa_{1-x}As} = 1.7 \times 10^{-4}$, 2.6×10^{-4} , and 3.7×10^{-4} atm at arsenic pressures ($P_{As_4}^0$) of 4.3×10^{-4} , 1.3×10^{-3} and 3.9×10^{-3} atm, respectively. The figures demonstrate that Eq. (13) describes the data accurately when one value of $P_{In_xGa_{1-x}As}$ is used at one arsenic pressure. The straight line indicates that changing the gallium monochloride pressures over the range indicated has little effect on the equilibrium amount of $In_xGa_{1-x}As$ deposited. These results clearly illustrate the fact that the equilibrium expression [Eq. (13)] can be used with confidence to interpret the deposition of the ternary in the 0.4-0.5 value range for 1-x.

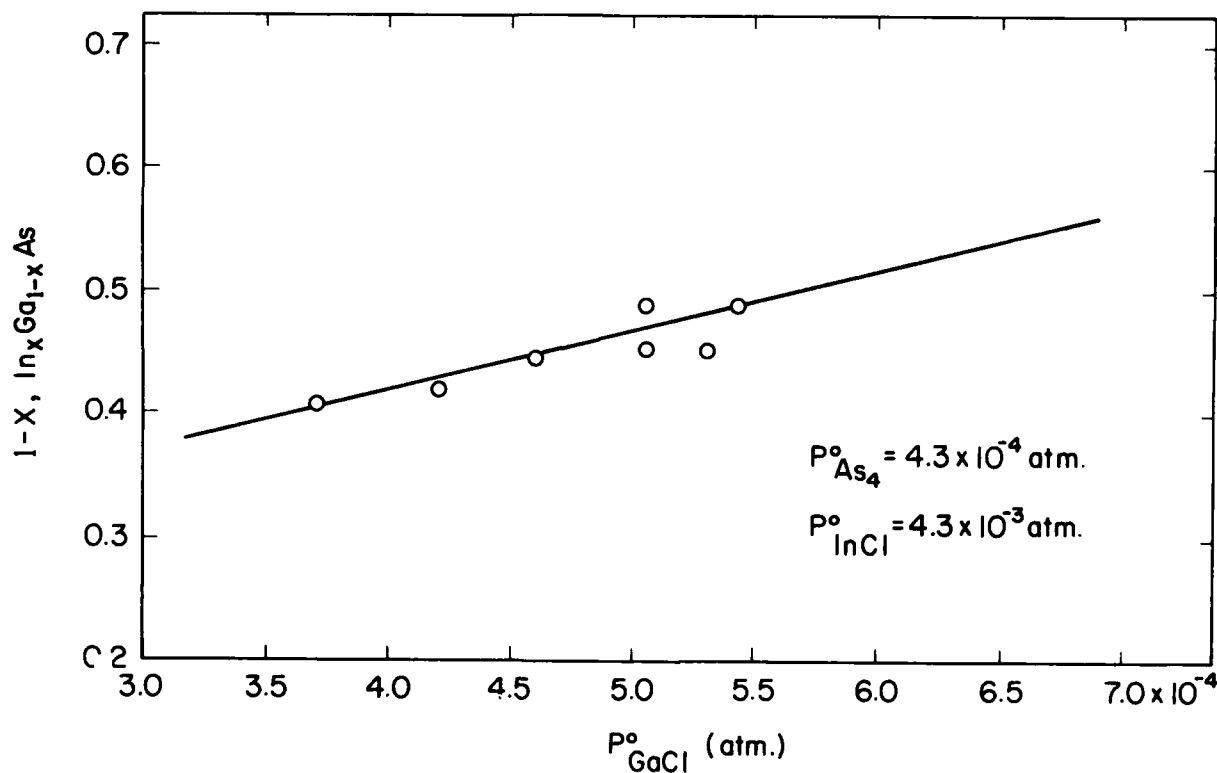


Figure 1. Mole Fraction of Gallium Arsenide, 1-x, in $In_xGa_{1-x}As$ as a Function of the Partial Pressure of Gallium Monochloride (P_{GaCl}^0). —: Calculated With Eq. (13) Using $P_{In_xGa_{1-x}As} = 1.7 \times 10^{-4}$ atm at $P_{As_4}^0 = 4.3 \times 10^{-4}$ atm. Experimental points are from Reference 20 and are indicated by O

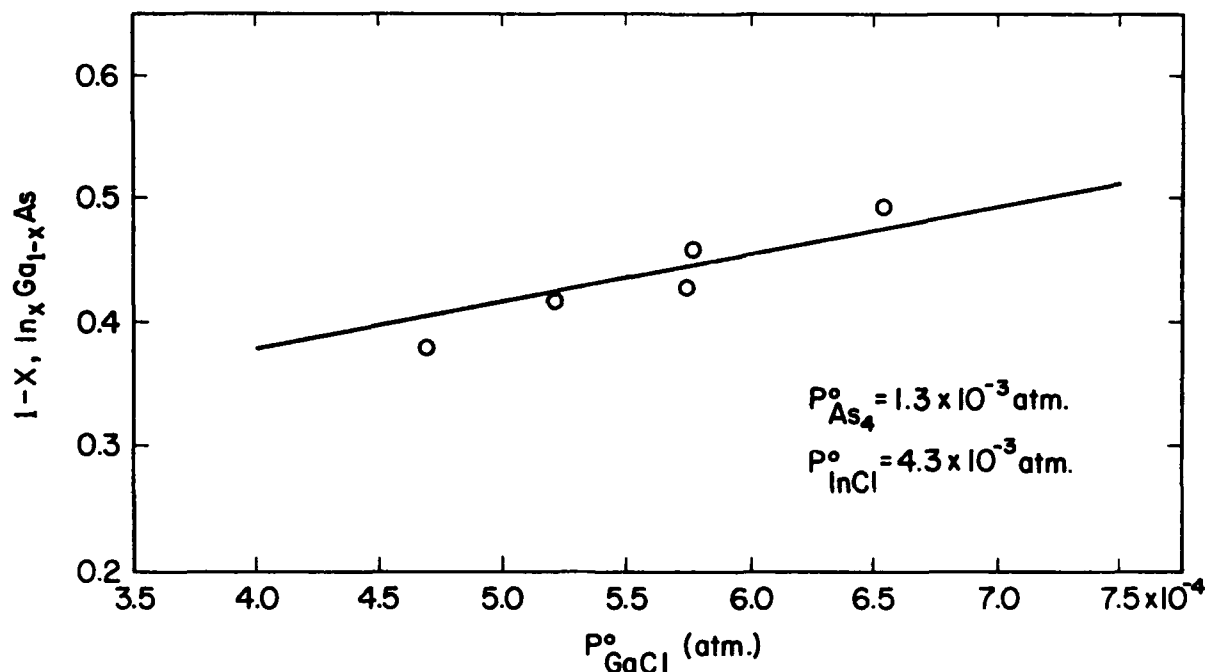


Figure 2. Mole Fraction of Gallium Arsenide, $1-x$, in $\text{In}_x\text{Ga}_{1-x}\text{As}$ as a Function of the Partial Pressure of Gallium Monochloride (P_{GaCl}^0). —: Calculated With Eq. (13) Using $P_{\text{In}_x\text{Ga}_{1-x}\text{As}} = 2.6 \times 10^{-4}$ atm at $P_{\text{As}_4}^0 = 1.3 \times 10^{-3}$ atm. Experimental points are from Reference 20 and are indicated by O

Curve fitting of Eq. (13) with the experimental data shows that increasing the arsenic pressure increases the equilibrium amounts of $\text{In}_x\text{Ga}_{1-x}\text{As}$ that are deposited. This is not surprising since equilibrium considerations mandate this chemical behavior. The calculated equilibrium amounts of $\text{In}_x\text{Ga}_{1-x}\text{As}$ deposited as a function of the initial arsenic pressures are exhibited in Figure 4. A straight line is drawn through the data points that enables values of $P_{\text{In}_x\text{Ga}_{1-x}\text{As}}$ to be determined at any partial pressure of $P_{\text{As}_4}^0$. The data points in Figure 4 indicate a slight parabolic trend as implied by Eq. (13), $(P_{\text{As}_4}^0)^{1/4} = f[P_{\text{In}_x\text{Ga}_{1-x}\text{As}}]$; calculations with the linear relationship at low $P_{\text{As}_4}^0$ values gave more acceptable values.

The calculated lines in Figures 1, 2 and 3 extend over a limited range of gallium monochloride pressures. Figure 5 illustrates the effect of extending the partial pressures of gallium monochloride on x , the mole fraction of indium arsenide at

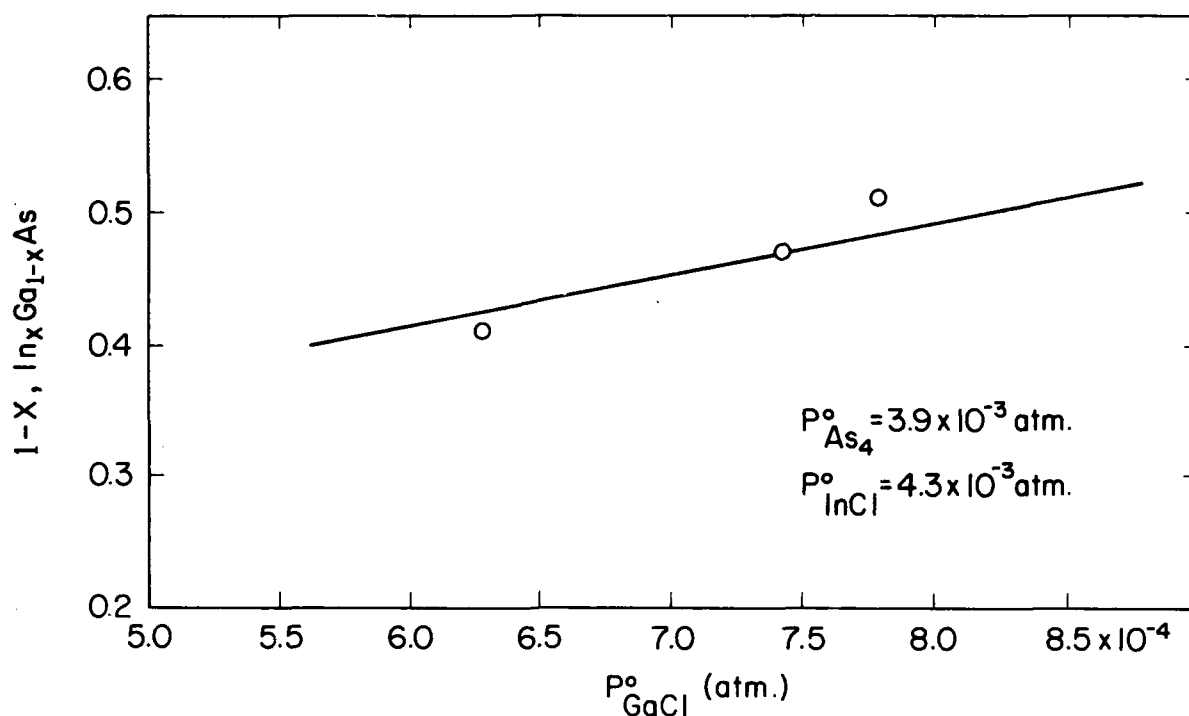


Figure 3. Mole Fraction of Gallium Arsenide, $1-x$, in $In_xGa_{1-x}As$ as a Function of the Partial Pressure of Gallium Monochloride (P_{GaCl}^o). —: Calculated With Eq. (13) Using $P_{In_xGa_{1-x}As} = 3.7 \times 10^{-4}$ atm at $P_{As_4}^o = 3.9 \times 10^{-3}$ atm. Experimental points are from Reference 20 and are indicated by O

two $P_{As_4}^o$. Values of x are plotted as a function of the ratio of the partial pressure of InCl to the total III-monochloride pressures $\left(\frac{P_{InCl}^o}{P_{GaCl}^o + P_{InCl}^o} \right)$. The partial pressure of InCl was held constant at 4.3×10^{-3} atm and that of GaCl was varied from 1.9×10^{-3} to 4.4×10^{-5} atm. The figure shows that decreasing the partial pressure of GaCl by approximately 2.5X decreases the mole fraction of Ga in $In_xGa_{1-x}As$ by ~13 percent. These curves are similar to those reported by Kajiyama.¹⁴ The data of Conrad et al²³ and Enstrom et al²⁴ are plotted to show

23. Conrad, R.W., Hoyt, P.L., and Martin, D.D. (1967) Preparation of epitaxial $Ga_xIn_{1-x}As$, J. Electrochem. Soc. 114:164.
24. Enstrom, R.E., Richman, D., Abrahams, M.S., Appert, J.R., Fisher, D.G., Sommers, A.H., and Williams, B.F. (1970) Vapour growth of $Ga_{1-x}In_xAs$ for infrared photocathode applications, Proc. 3rd Int. Symp. on Gallium Arsenide, Conf. Series Number 9, Inst. of Phys., Aachen, Germany, pp. 30-40.

that the present method of analysis accurately describes the trend of the experimental values of other investigators. The deposition temperatures used by these investigators are higher (725 and 745°C) than the temperature of 700°C used in the present study. Figure 5 shows that at high GaCl partial pressures ($P_{\text{GaCl}}^0 > 1.9 \times 10^{-3}$ atm), the mole fraction of indium arsenide (x) calculated by the present method approaches zero rather abruptly. This is different from the experimental results where x slowly approaches zero. A possible explanation for this difference is that the equilibrium amounts of $\text{In}_x\text{Ga}_{1-x}\text{As}$ deposit do not remain constant but increases at high GaCl partial pressures.

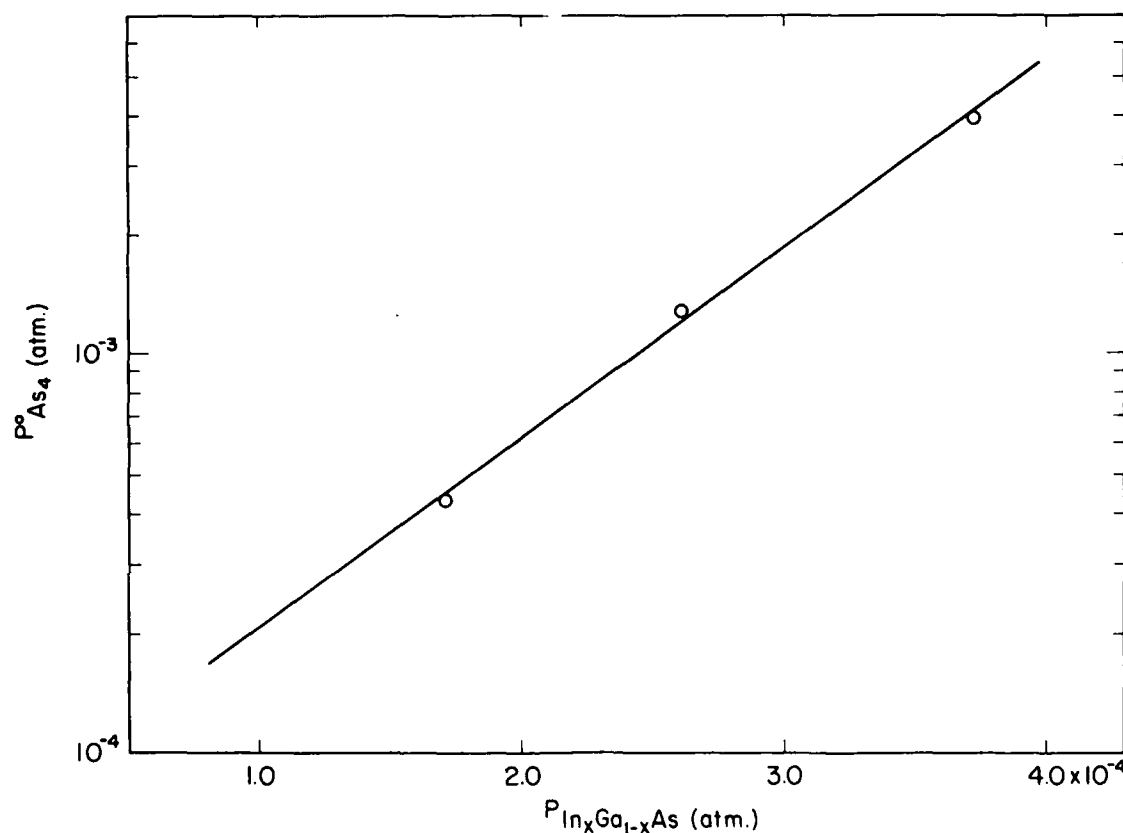


Figure 4. Calculated Equilibrium Values of $\text{In}_x\text{Ga}_{1-x}\text{As}$ Deposited ($P_{\text{In}_x\text{Ga}_{1-x}\text{As}}$ atm) Versus Initial Arsenic Partial Pressures ($P_{\text{As}_4}^0$). $P_{\text{In}_x\text{Ga}_{1-x}\text{As}}$ Values are Calculated Using Eq. (13) (see text)

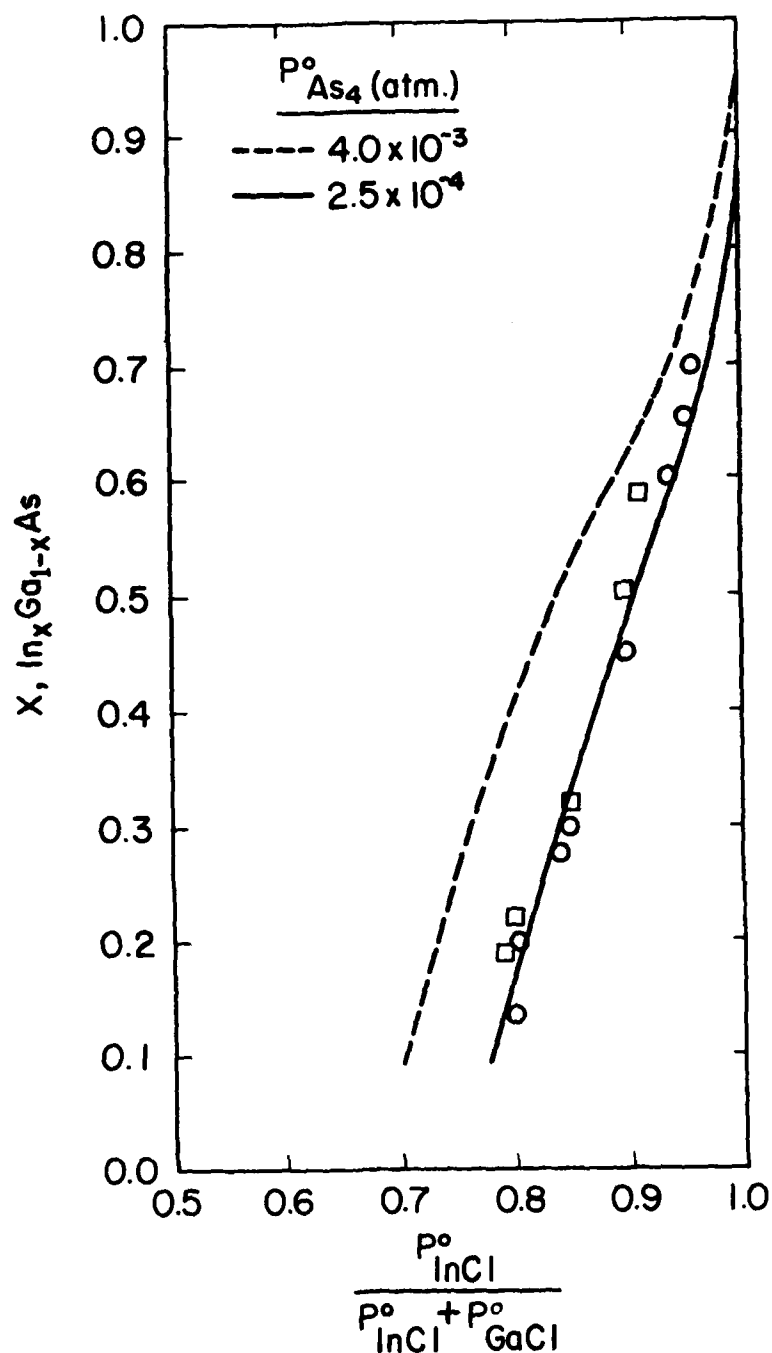


Figure 5. Calculated Mole Fraction of Indium Arsenide, x , in $In_xGa_{1-x}As$ as a Function of the Ratio of the Initial Partial Pressure of Indium Monochloride to the Total Partial Pressure of III-Monochlorides ($P_{InCl}^0 / P_{InCl}^0 + P_{GaCl}^0$). Experimental values are from References 23 and 24. Those from Reference 23 are indicated by O; those from Reference 24 are indicated by \square .

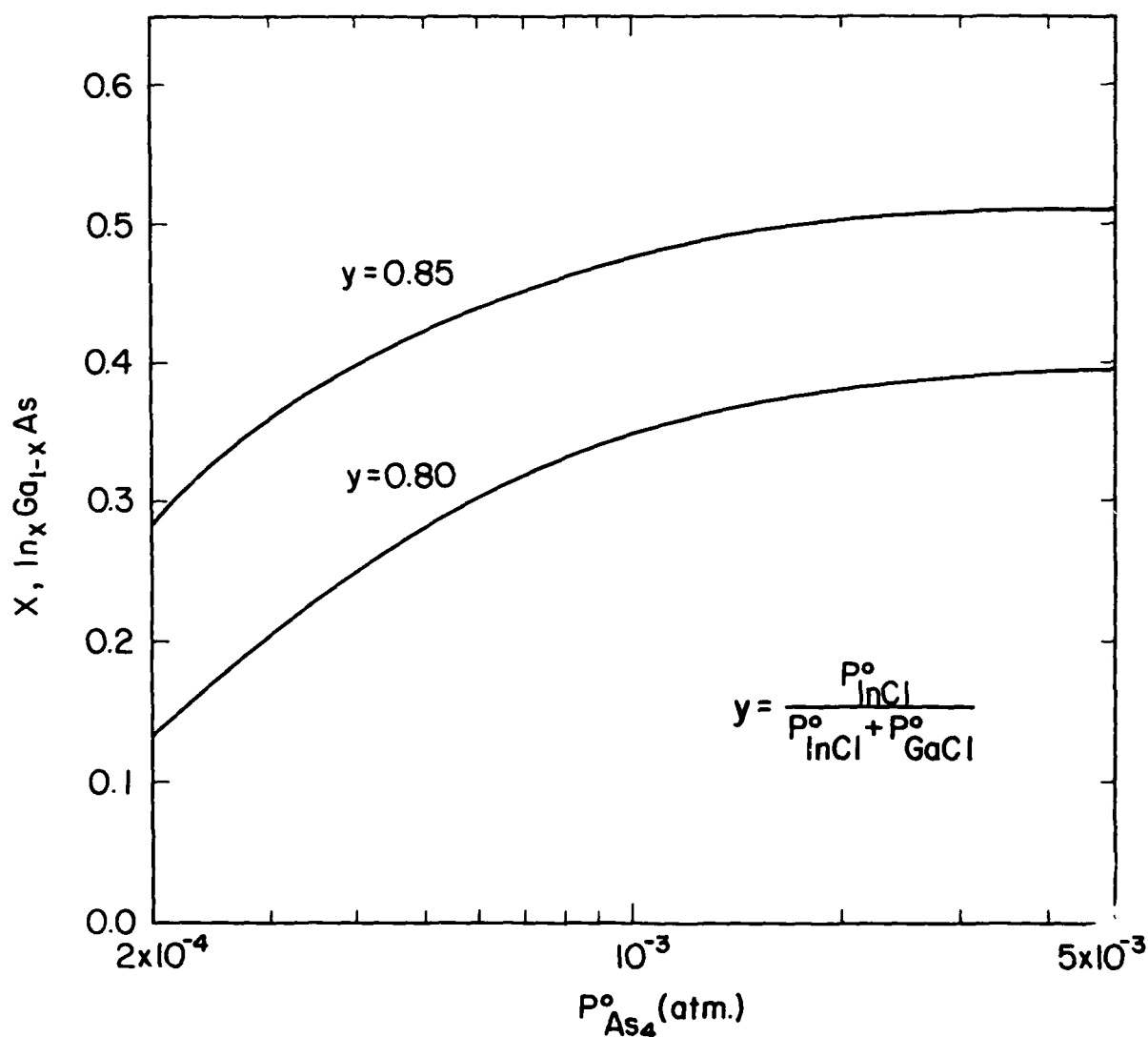


Figure 6. Calculated Variation of Indium Arsenide Mole Fraction, x , in $\text{In}_x\text{Ga}_{1-x}\text{As}$ as a Function of the Initial Partial Pressures of Arsenic

$(P_{\text{As}_4}^0)$ at Two $\frac{P_{\text{InCl}}^0}{P_{\text{InCl}}^0 + P_{\text{GaCl}}^0}$ Values

The effect of arsenic pressure on the composition of the ternary is observed in Figure 5. The mole fraction(x) of indium arsenide is increased in the ternary with increasing arsenic partial pressures. This effect is shown more dramatically in Figure 6 where $P_{\text{As}_4}^0$ is plotted against the mole fraction(x) of indium arsenide in the ternary at constant GaCl and InCl partial pressure. With increasing $P_{\text{As}_4}^0$, the

mole fraction of indium arsenide increases until a value is obtained that remains constant with further increases in arsenic pressure. Experimental studies have not been reported at these high $P_{As_4}^0$ to see whether constant indium arsenide mole fractions are observed. The method proposed by Jacobs et al.¹⁶ and Kajiyama¹⁴ show the indium arsenide mole fraction remains constant at high $P_{As_4}^0$ values while that of Nagai¹⁵ indicates an increase in indium arsenide mole fraction with increasing arsenic pressures. The present method derived from experimental data clearly shows that increasing arsenic pressures increases the indium arsenide in $In_xGa_{1-x}As$. A possible explanation for this observation is that as the pressure of As_4 increases, the number of collisions between indium atoms and As_4 molecules increases resulting in an increase in the number of effective collisions. The effective collision number between Ga and As_4 probably remains maximum even at low As_4 pressures. This difference in chemical reactivity gives rise to $In_xGa_{1-x}As$ containing greater amounts of indium at high As_4 pressures.

The present method is valuable only if the composition of the ternary can be predicted from the reactants' partial pressures. Table 1 shows the compositions of $In_xGa_{1-x}As$ calculated with the present method along with those determined experimentally by Hyder et al.²⁵ and Jacobs et al.¹⁶ Exceptionally good agreement is observed if one considers the variability that each reactor demonstrates. Although the deposition temperatures of Hyder et al (688°C) and Jacobs et al (727°C) are different from the temperature (700°C) used in the calculations, the results illustrate that this temperature difference has little effect in the present comparison. Not all the experimental data studied by the present method gave such good agreement as reported in Table 1. For example, Macrander and Strege¹¹ reported initial partial pressures of GaCl, InCl and AsH_3 to prepare $In_{0.53}Ga_{0.47}As$. Using these same values, the present method gave a ternary composition corresponding to $In_{0.34}Ga_{0.66}As$. This difference in composition can be attributed to a number of factors, such as reactor characteristics, errors associated with mass flow controllers, and errors in analyses of gas mixtures. The value of the present method lies in its ability to determine with simplicity the partial pressures of GaCl, InCl, and AsH_3 to be used in preparing a desired composition of a ternary, for example $In_{0.53}Ga_{0.47}As$.

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Table 1. Comparison of Experimental x Values ($\text{In}_x\text{Ga}_{1-x}\text{As}$) With Those Calculated by the Present Method

Sample	Experimental x	Calculated x (Present Method)	Reference
22-1	0.53	0.52	Hyder et al ²⁵
18-22	0.53	0.46	Hyder et al ²⁵
24-2	0.53	0.59	Hyder et al ²⁵
Fig. 1	0.54	0.59	Jacobs et al ¹⁶
Fig. 1	0.55	0.60	Jacobs et al ¹⁶
Fig. 1	0.52	0.59	Jacobs et al ¹⁶

4. CONCLUSIONS

A method has been developed to estimate the composition of the ternary, $\text{In}_x\text{Ga}_{1-x}\text{As}$, prepared by the VPE-hydride technique. The method requires knowledge of the equilibrium amounts of $\text{In}_x\text{Ga}_{1-x}\text{As}$ deposited. A plot is given where equilibrium amounts of $\text{In}_x\text{Ga}_{1-x}\text{As}$ deposited can be determined at any initial arsenic pressure. The composition of the ternary is estimated from the initial partial pressures of the reactants and the amount of $\text{In}_x\text{Ga}_{1-x}\text{As}$ deposited. Comparison of the results derived from the present method with experimental compositions exhibited good agreement. The method may be applied to other ternary systems, for example, $\text{In}_x\text{Ga}_{1-x}\text{P}$, to understand their deposition process.

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